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PASSIVATION OF SEMICONDUCTOR SURFACES FOR IMPROVED RADIATION DETECTORS: X-RAY PHOTOEMISSION ANALYSIS

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ABSTRACT

Surface passivation of device-grade radiation detector materials was investigated using x-ray photoelectron spectroscopy in combination with transport property measurements before and after various chemical treatments. Specifically Br-MeOH (2% Br), KOH with $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ and NH_4OH solutions were used to etch, reduce and oxidize the surface of $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$ semiconductor crystals. Scanning electron microscopy was used to evaluate the resultant microscopic surface morphology. Angle-resolved high-resolution photoemission measurements on the valence band electronic structure and core lines were used to evaluate the surface chemistry of the chemically treated surfaces. Metal overlayers were then deposited on these chemically treated surfaces and the I-V characteristics measured. The measurements were correlated to understand the effect of interface chemistry on the electronic structure at these interfaces with the goal of optimizing the Schottky barrier height for improved radiation detector devices.

INTRODUCTION

The development of cadmium zinc telluride ($\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$, CZT) as a nuclear radiation detector material has progressed with advances in CZT crystal growth that minimizes bulk defects and precipitates.[1,2] With this progress, our focus is now on surface properties of CZT since the interfacial chemistry has a powerful influence on the electrical stability of ohmic and Schottky contacts to CZT. The performance of CZT as a room temperature radiation detector can thus be improved with careful attention to modification of the surface chemistry. Chemical treatments of the CZT surface prior to application of electrical contacts require comprehensive characterization to elucidate advantageous changes in surface electronic structure.

Mechanical polishing followed by bromine-based etching is routinely employed for CZT surface preparation prior to device fabrication. This treatment removes the native oxide but leaves a Te-rich surface resulting in metal/CZT interface degradation and excessive leakage currents. [1-3] Alternative surface preparation methods have been proposed for surface passivation [3-6] but have not been fully characterized nor implemented for practical device fabrication.

This paper presents the results from an investigation of the surface chemistry, surface morphology and electronic structure of chemically treated $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$ and correlates the results with transport properties.

EXPERIMENT

Device-grade $p\text{-Cd}_{(1-x)}\text{Zn}_x\text{Te}$ was polished and subjected to various chemical treatments. Initially a 2 min Br-MeOH (2% Br) etch was performed and the resultant surface chemistry was

characterized by x-ray photoelectron spectroscopy (XPS). Alternatively, following Br:MeOH etching, the CZT was treated with KOH (15 % in water) for 40 min, rinsed with DI water, then subjected to $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ (10%/10% in water) for 45 min, rinsed again with DI water and blown dry. Concentrated NH_4OH was also used to treat the oxidized CZT surface for 2 min at ambient temperature.

XPS analysis was performed on a PHI Quantum 2000 system using a focused monochromatic Al $\text{K}\alpha$ x-ray (1486.7 eV) source for excitation and a spherical section analyzer. The instrument has a 16-element multichannel detection system. A 200 μm diameter x-ray beam was used for analysis. The x-ray beam is incident normal to the sample and the x-ray detector is at 45° away from the normal. The pass energy was 23.5 eV giving an energy resolution of 0.3 eV that when combined with the 0.85 eV full width at half maximum (FWHM) Al $\text{K}\alpha$ line width gives a resolvable XPS peak width of 1.2 eV FWHM. Deconvolution of non-resolved peaks was accomplished using Multipak 6.1A (PHI) curve fitting routines. The collected data were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at 932.72 ± 0.05 eV and Au $4f_{7/2}$ at 84.01 ± 0.05 eV. Binding energies were also referenced to the C 1s photoelectron line arising from adventitious carbon at 284.8 eV. Low energy electrons and argon ions were used for specimen neutralization.

Diodes were fabricated by depositing platinum top contacts with guard rings and a gold backside contact. Current versus voltage measurements were performed on these diodes to determine the effect of contact interface chemistry on detector transport properties.

RESULTS AND DISCUSSION

XPS survey spectra of the etched, reduced and oxidized surfaces of $p\text{-Cd}_{(1-x)}\text{Zn}_x\text{Te}$ were acquired to determine surface stoichiometry and impurity concentrations. The quantitative surface compositional analyses and elemental ratios are summarized in Table I. Cd/Te ratio indicates that (1) 2%Br:MeOH etch results in a Te-rich surface, (2) KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment results in a stoichiometric surface, and (3) NH_4OH results in a Te-rich surface.

Table I. Relative XPS Surface Compositional Analysis (atomic %) of the Chemically Treated $\text{Cd}_{(1-x)}\text{Zn}_x\text{Te}$

Sample	Cd	Zn	Te	Cd/Te
CZT, as received	50.7	2.0	47.3	1.07
CZT – 2%Br:MeOH etch	31.6	2.0	66.4	0.48
CZT - KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment	50.5	-	49.5	1.02
CZT - NH_4OH treatment	40.9	1.7	57.4	0.71

High magnification planar view scanning electron microscopy (SEM) photomicrographs are presented in Figure 1(a) and (b), respectively, of the Br:MeOH etched and KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treated CZT surfaces. The observed morphology on the surface of the Br:MeOH etched CZT has an orange peel texture. The surface morphology of the KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$

treated CZT surface shows some pitting in addition to the formation of a thin surface oxide (≈ 10 nm).

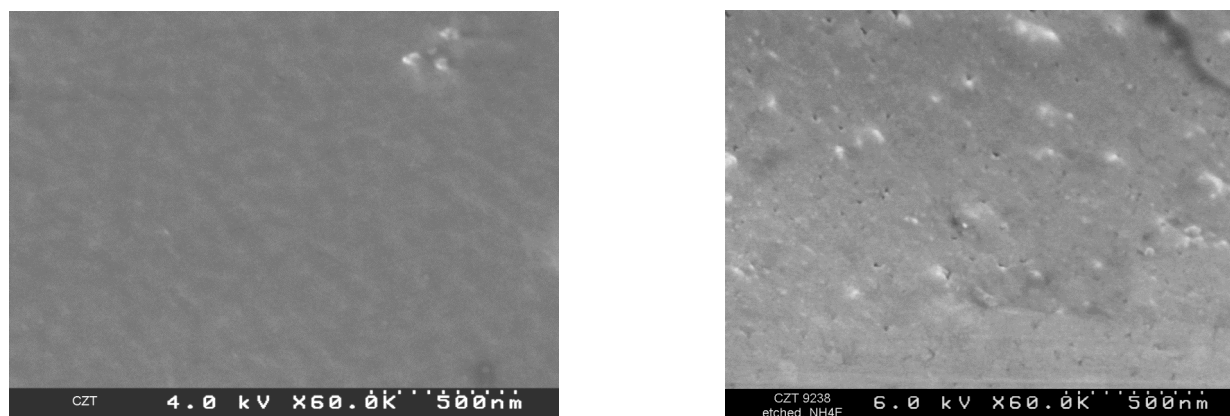


Figure 1. SEM photomicrographs of (a) Br:MeOH etched CZT and (b) KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treated CZT.

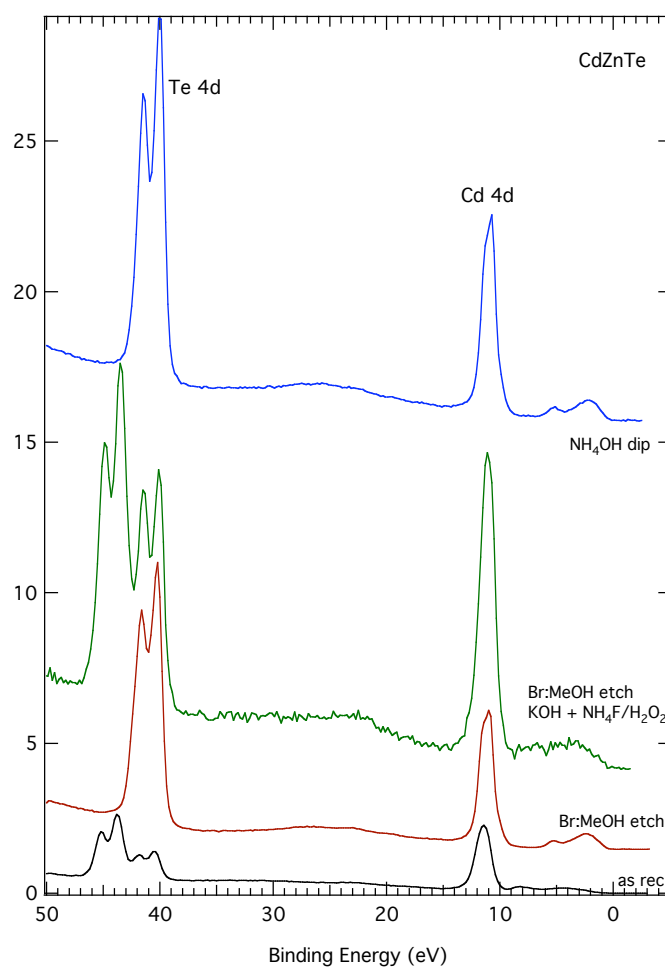


Figure 2. XPS core-level and valence band spectra for the etched and treated CZT surfaces.

Figure 2 shows the shallow core-levels and valence band region for the as received, Br:MeOH etched, KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treated, and NH_4OH etched CZT surfaces. These spectra contain the Te 4d, Cd 4d and upper valence band, and provide unique information about the electronic structure and the nature of chemical bonding at the CZT surface. The evolution of the electronic structure at the surface is indicated by the transition of the valence band maximum (VBM).

In these spectra, the Te $4d_{5/2,3/2}$ core-level has two spin-orbit pairs. The higher binding energy spin-orbit pair at 43.8 eV and 45.0 eV represent an oxide ($\text{TeO}_2/\text{CdTeO}_3$) and the lower binding energy pair at 40.6 eV and 41.8 eV represents Te in CZT in agreement with literature values. [7] The Cd 4d spin-orbit pair cannot be resolved with our instrumentation, so the measured centroid of this peak is at 11.4 eV. In addition, the full width half maximum (FWHM) of the Cd 4d peak indicates the presence of a surface oxide (CdTeO_3) for as received CZT. Following the Br:MeOH etch the Te 4d oxide components disappear indicating removal of the native oxide. Also, Te $4d_{5/2,3/2}$ the spin-orbit pair and the Cd 4d peak shifts 0.4 eV to lower binding energy. In addition, the intensity of the Te 4d peaks increases relative to the Cd 4d intensity further supporting the presence of a Te-rich surface, possibly with the formation of Te islands. Formation of Te islands would account for the increased Te signal relative to the Cd signal due to the visibility of the substrate between the islands.

Following KOH + $\text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment, the Te $4d_{5/2,3/2}$ core-level spectra show two component pairs and the Cd 4d core line broadens indicating oxide formation. The energy shifts observed for the Te $4d_{5/2,3/2}$ spin-orbit components following this peroxide treatment is similar to those observed for the Cd 4d core level. Also note that the relative intensity ratio of the Te 4d and Cd 4d has change. Recall that compositional analysis determined this to be a stoichiometric surface. Electrical contacts are deposited on this oxide surface for the following transport property measurements.

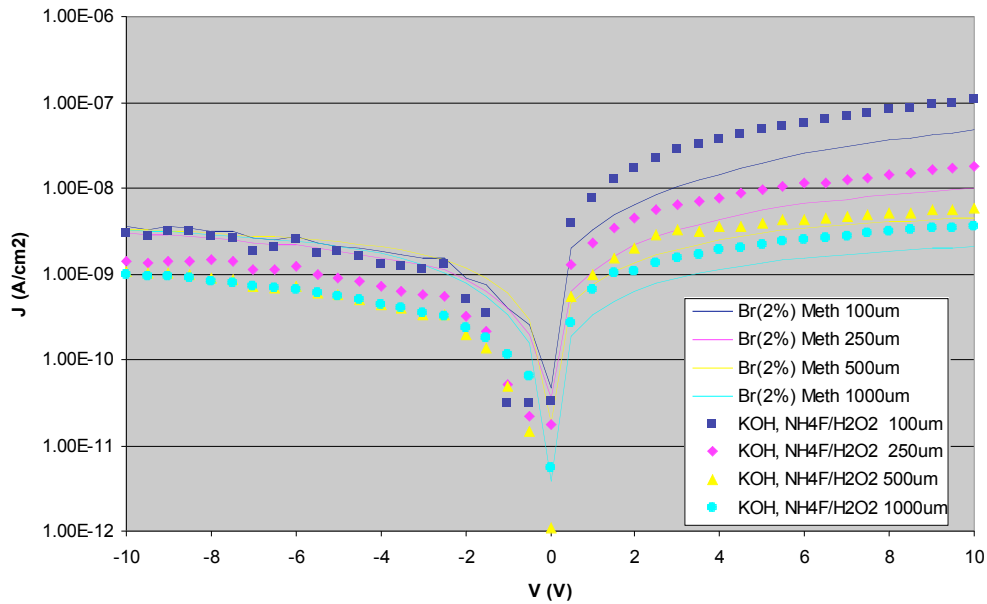


Figure 3. Characteristic I-V curves of the Pt/CZT/Au diodes as a function of surface treatment and Pt contact size.

The final surface chemical treatment we explored was a NH_4OH dip at ambient temperature for 2 min. The resulting Te 4d and Cd 4d spectrum reveals that the oxide was removed by this treatment. Again note the change in the relative intensity ratio of the Te 4d and Cd 4d supporting the compositional analysis that indicated this is a Te-rich surface. This treatment could be a replacement for the standard Br:MeOH etch for future CZT device fabrication.

Representative current versus voltage curves (log scale) for the diodes with guard rings are shown in Fig. 3. Rectifying behavior was achieved for the device. Note that the forward current does not scale with diode area, possibly due to a high series resistance issue. In addition, observe that there is a larger forward to reverse current ratio for $\text{KOH} + \text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treated samples versus the Br:MeOH etched samples. The measured resistivity (-10 V effective reverse bias) is 1.6×10^{10} ohm-cm for the Br:MeOH etch versus 5.5×10^{10} ohm-cm for $\text{KOH} + \text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment.

CONCLUSIONS

X-ray photoelectron spectroscopy has been used to determine the effects of wet chemical etching/treatment on the surface chemistry and surface electronic structure of CZT. Results show that 2% Br:MeOH removes the surface oxide and that the $\text{KOH} + \text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment yields a well-behaved oxide surface. The NH_4OH treatment resulted in an oxide free surface and may be a preferred surface preparation treatment for CZT devices. The I-V characteristics reveal that $\text{KOH} + \text{NH}_4\text{F}/\text{H}_2\text{O}_2$ treatment produces better blocking characteristics and lower reverse leakage currents. Future work will include treating CZT with $(\text{NH}_4)_2\text{S}$ and NH_4OH /thiourea solutions and measuring I-V/C-V characteristics.

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